

<b>REPORT DOCUMENTATION PAGE</b>			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 15-10-2015		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 7-Jul-2014 - 6-Jul-2015	
4. TITLE AND SUBTITLE Final Report: Environmentally Controlled Infrared Spectroscopy System for Fundamental Studies of Polymer Electrolyte Membranes			5a. CONTRACT NUMBER W911NF-14-1-0365		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611102		
6. AUTHORS Jonathan Doan, Andy Vong, Neili Loupe, Kierstyn Anderson, Erin Kingston, Cassandra Johnson, Nilufar Nasirova, Eugene S Smotkin			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES Northeastern University 360 Huntington Avenue 490 RP Boston, MA 02115 -5005			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 65070-CH-RIP.4		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT Dehydration studies of ionomer (Nafion and SPEEK) membranes were accomplished using a high pressure/ high temperature infrared cell. Categorization of ionomer exchange site normal modes by exchange site local symmetry enabled correlation of the exchange site structure to state-of-hydration. Polarization modulated infrared reflection-absorption spectroscopy experiments are enabled by the use of a spin-coater to coat SiO2 and Pt surfaces with ionomer solutions. PM-IRRAS allows for the determination of what ionomer functional groups are ordered by the Pt surface and are involved in adsorption. Also, the ionomer membranes are being used in a specialized reaction.					
15. SUBJECT TERMS SPEEK, Nafion, Ionomers, state-of-hydration, infrared spectroscopy					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Eugene Smotkin
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 617-373-7526



## Report Title

Final Report: Environmentally Controlled Infrared Spectroscopy System for Fundamental Studies of Polymer Electrolyte Membranes

### ABSTRACT

Dehydration studies of ionomer (Nafion and SPEEK) membranes were accomplished using a high pressure/ high temperature infrared cell. Categorization of ionomer exchange site normal modes by exchange site local symmetry enabled correlation of the exchange site structure to state-of-hydration. Polarization modulated infrared reflection-absorption spectroscopy experiments are enabled by the use of a spin-coater to coat SiO<sub>2</sub> and Pt surfaces with ionomer solutions. PM-IRRAS allows for the determination of what ionomer functional groups are ordered by the Pt surface and are involved in adsorption. Also, the ionomer membranes are being used in a specialized reaction system, where olefins are isomerized and analyzed using a gas chromatograph-mass spectrometer. By varying the reaction cell potential, the catalyst acidity can be tuned.

---

**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
10/09/2015	1.00 Erin Kingston, Ian Kendrick, Kierstyn Anderson, Jonathan Doan, Nicholas Dimakis, Philippe Knauth, Maria Luisa Di Vona, Eugene S. Smotkin. Theoretical and experimental infrared spectra of hydrated and dehydrated sulfonated poly(ether ether ketone), Polymer, (09 2014): 4671. doi: 10.1016/j.polymer.2014.07.011
10/09/2015	2.00 Jonathan Doan, Nestor E. Navarro, Dunesh Kumari, Kierstyn Anderson, Erin Kingston, Cassandra Johnson, Andy Vong, Nicholas Dimakis, Eugene S. Smotkin. Symmetry-based IR group modes as dynamic probes of Nafion ion exchange site structure, Polymer, (09 2015): 34. doi: 10.1016/j.polymer.2015.07.017
<b>TOTAL:</b>	<b>2</b>

**Number of Papers published in peer-reviewed journals:**

---

**(b) Papers published in non-peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
<b>TOTAL:</b>	

**Number of Papers published in non peer-reviewed journals:**

---

**(c) Presentations**

Smotkin, E.S.; Doan, J.; Kingston, E.; Anderson, K.; Vong, A. Theoretical and experimental vibrational spectroscopy of ionomers. Presented at the 249th ACS National Meeting & Exposition, Denver, CO, March 22-26, 2015. PMSE 473.

Anderson, K.; Kingston, E.; Smotkin, E.S. IR Spectroscopy of Cd<sup>2+</sup> exchanged Nafion and sulfonated poly(ether ether ketone), vs. state-of-hydration, for quantum dot preparation. Presented at the 249th ACS National Meeting & Exposition, Denver, CO, March 22-26, 2015. PMSE 476.

Romeo, J.; Doan, J.; Vong, A.; Smotkin, E. S. Composite sulfonated polyether ether ketone (SPEEK) proton exchange membranes for automotive fuel cells. Presented at the 250th ACS National Meeting & Exposition, Boston, MA, August 16-20, 2015. PMSE 388.

Vong, A.; Kendrick, I.; Doan, J.; Smotkin, E. S. Voltage tuned acidity of catalyst surfaces for non-faradaic isomerization reactions. Presented at the 250th ACS National Meeting & Exposition, Boston, MA, August 16-20, 2015. CHED 52.

**Number of Presentations:** 4.00

---

**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

<u>Received</u>	<u>Paper</u>
-----------------	--------------

**TOTAL:**

**Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

---

**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

<u>Received</u>	<u>Paper</u>
-----------------	--------------

**TOTAL:**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received      Paper

TOTAL:

Number of Manuscripts:

Books

Received      Book

TOTAL:

Received      Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

---

### Graduate Students

NAME

PERCENT SUPPORTED

**FTE Equivalent:**

**Total Number:**

---

### Names of Post Doctorates

NAME

PERCENT SUPPORTED

**FTE Equivalent:**

**Total Number:**

---

### Names of Faculty Supported

NAME

PERCENT SUPPORTED

**FTE Equivalent:**

**Total Number:**

---

### Names of Under Graduate students supported

NAME

PERCENT SUPPORTED

**FTE Equivalent:**

**Total Number:**

---

### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 1.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: ..... 0.00

---

### Names of Personnel receiving masters degrees

NAME

**Total Number:**

**Names of personnel receiving PhDs**

<u>NAME</u> Jonathan Doan <b>Total Number:</b>	<b>1</b>
--	----------

**Names of other research staff**

<u>NAME</u>  <b>FTE Equivalent:</b> <b>Total Number:</b>	<u>PERCENT SUPPORTED</u>
---	--------------------------

**Sub Contractors (DD882)**

**Inventions (DD882)**

## Scientific Progress

### 1) Statement of the problem studied

Infrared (IR) spectroscopy is ideal for the study of ionomer membranes in terms of state-of-hydration and ion-exchange. Our lab has developed a method of IR normal mode assignment based on the local symmetry of the ionomer exchange site. The use of the SPECAC high pressure/high temperature cell enabled time-dependent spectroscopy of the ionomer membrane during dehydration. Previously we have identified certain IR bands (1061 cm<sup>-1</sup> and 969 cm<sup>-1</sup>) in hydrated Nafion (corresponding to a local C3V exchange site symmetry). When the membrane is dehydrated, the C3V bands diminish while a pair of other bands (1414 cm<sup>-1</sup> and 910 cm<sup>-1</sup>) corresponding to a local C1 exchange site symmetry (dehydrated state). The combination of vacuum and heat during dehydration allowed us to reach levels of rigorous dehydration never before achieved. The spectra of fully dehydrated Nafion was published in Doan et al. [1] (Fig. 2). This is the first time complete disappearance of the 1061 cm<sup>-1</sup> band has been observed.

### 2) Summary of the most important results

The SPECAC cell was used in the ion-exchanged, state-of-hydration membrane studies. The results were published in Polymer [1]. Metal ions (M) with  $\Delta_{\text{hyd}}$  below 550 kJ/mol alter the exchange site at all states-of-hydration. They bind with C3V symmetry and exhibit high orbital overlap with the sulfonate sulfur and oxygen atoms. The Nafion-[H] C3V,LF (primarily sulfonate stretching) vanishes at full dehydration with retention of the C3V,HF (primarily ether link stretching). Theoretical Nafion-[M] C3V, LF bands (e.g., 940 cm<sup>-1</sup> for Li<sup>+</sup>) are not experimentally observed. Hydration waters of ions with  $\Delta_{\text{hyd}} > 1800$  kJ/mol cannot be displaced by sulfonate oxygens. Thus, the Nafion-[H] C3V,LF persists at all states of hydration.

Funds were also used to purchase a spin coater which has been used to spin ionomer thin films (Nafion, SPEEK, and alkaline FAA-3) onto SiO<sub>2</sub> and Pt wafer surfaces. These samples can then be used for different types of reflectivity measurements, which include polarization modulated infrared reflection absorption spectroscopy, X-ray reflectometry, and neutron reflectometry. In PM-IRRAS, the combination of electric field enhancement and the surface selection rule, allows us to determine which functional groups are ordered by adsorption to the surface. The IR normal modes that have a transition moment perpendicular to the surface are enhanced. Previous results show that the SO<sub>3</sub>- group and CF<sub>3</sub> groups are involved in the self-assembly of Nafion on Pt. [2] This is in contrast to SPEEK, which does not have the flexible side chain functional groups that Nafion contains. Instead the SO<sub>3</sub>- group is located directly on the aromatic backbone, limiting the mobility of the hydrophilic/hydrophobic phase separation. PM-IRRAS of SPEEK thin films on Pt shows the enhancement of backbone normal modes, particularly COC stretching. Interestingly, at this stage we do not see much PM-IRRAS enhancement SO<sub>3</sub>- contribution to the interface. Neutron reflectometry results obtained at the NIST Center for Neutron Research in Gaithersburg, MD are currently being fitted (SPEEK on Pt and SiO<sub>2</sub>, FAA-3 on Pt).

The Agilent GC is currently being used to analyze results of a project involving isomerization of olefins through a flow reactor fuel cell. Typically, H<sub>2</sub> is flowed through the anode of a fuel cell and O<sub>2</sub> is flowed through the cathode of the fuel cell. The H<sub>2</sub> dissociates into protons and electrons, with the protons travelling through an ionomer membrane (e.g., Nafion or SPEEK) to the cathode and the electrons travelling through an external circuit. The protons and electrons combine with the O<sub>2</sub> at the cathode, producing current. In our setup, olefins are flowed through the cathode, where the protons are present at the catalytic layer. The olefins adsorb onto Pd and the protons cause isomerization, in the form of shifting double bonds, methyl groups, etc. The results are analyzed using the GC that was purchased from the grant funding. Preliminary results show isomerization of 2 methyl 2 pentene, but we are in the process of reproducing the results and developing a better method of sampling to the GC.

### 3) Bibliography

1. Doan J, Navarro NE, Kumari D, Anderson K, Kingston E, Johnson C, Vong A, Dimakis N, and Smotkin ES. Polymer 2015; 73:34-41.
2. Kendrick I, Kumari D, Yakaboski A, Dimakis N, and Smotkin ES. Journal of the American Chemical Society 2010;132(49): 17611-17616.

## Technology Transfer



Abstract: Dehydration studies of ionomer (Nafion and SPEEK) membranes were accomplished using a high pressure/ high temperature infrared cell. Categorization of ionomer exchange site normal modes by exchange site local symmetry enabled correlation of the exchange site structure to state-of-hydration. Polarization modulated infrared reflection-absorption spectroscopy experiments are enabled by the use of a spin-coater to coat SiO<sub>2</sub> and Pt surfaces with ionomer solutions. PM-IRRAS allows for the determination of what ionomer functional groups are ordered by the Pt surface and are involved in adsorption. Also, the ionomer membranes are being used in a specialized reaction system, where olefins are isomerized and analyzed using a gas chromatograph-mass spectrometer. By varying the reaction cell potential, the catalyst acidity can be tuned.

### 1) Statement of the problem studied

Infrared (IR) spectroscopy is ideal for the study of ionomer membranes in terms of state-of-hydration and ion-exchange. Our lab has developed a method of IR normal mode assignment based on the local symmetry of the ionomer exchange site. The use of the SPECAC high pressure/high temperature cell enabled time-dependent spectroscopy of the ionomer membrane during dehydration. Previously we have identified certain IR bands (1061 cm<sup>-1</sup> and 969 cm<sup>-1</sup>) in hydrated Nafion (corresponding to a local C<sub>3v</sub> exchange site symmetry). When the membrane is dehydrated, the C<sub>3v</sub> bands diminish while a pair of other bands (1414 cm<sup>-1</sup> and 910 cm<sup>-1</sup>) corresponding to a local C<sub>1</sub> exchange site symmetry (dehydrated state). The combination of vacuum and heat during dehydration allowed us to reach levels of rigorous dehydration never before achieved. The spectra of fully dehydrated Nafion was published in Doan et al. [1] This is the first time complete disappearance of the 1061 cm<sup>-1</sup> band has been observed. (Fig. 1)

### 2) Summary of the most important results

The SPECAC cell was used in the ion-exchanged, state-of-hydration membrane studies. The results were published in Polymer [1]. Metal ions (M) with  $\Delta_{\text{hyd}}$  below 550 kJ/mol alter the exchange site at all states-of-hydration. They bind with C<sub>3v</sub> symmetry and exhibit high orbital overlap with the sulfonate sulfur and oxygen atoms. The Nafion-[H] C<sub>3v,LF</sub> (primarily sulfonate stretching) vanishes at full dehydration with retention of the C<sub>3v,HF</sub> (primarily ether link stretching). Theoretical Nafion-[M] C<sub>3v,LF</sub> bands (e.g., 940 cm<sup>-1</sup> for Li<sup>+</sup>) are not experimentally observed. Hydration waters of ions with  $\Delta_{\text{hyd}} > 1800$  kJ/mol cannot be displaced by sulfonate oxygens. Thus, the Nafion-[H] C<sub>3v,LF</sub> persists at all states of hydration.

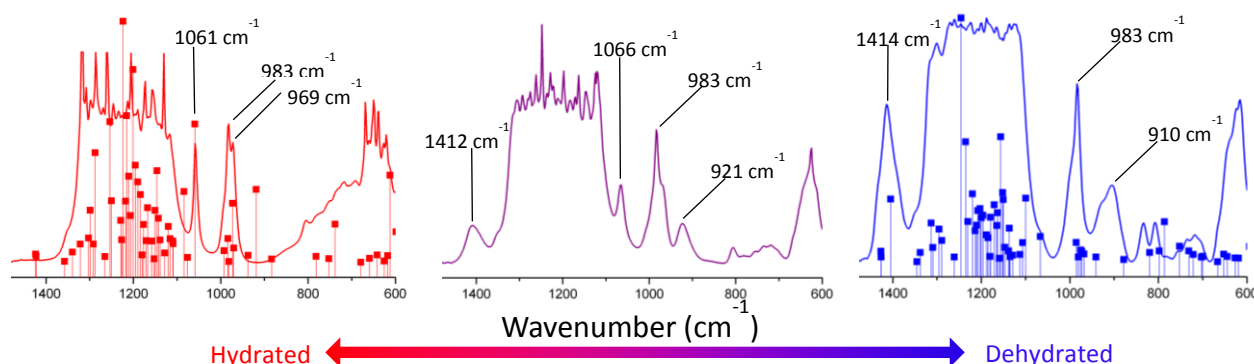


Figure 1. Nafion transmission spectra with overlaid DFT-calculated normal modes (drop lines). Spectra are plotted as normalized absorbance. Left: Hydrated Nafion-(H) (red). Middle: Partially dehydrated Nafion-H (purple). Right: Dehydrated Nafion-H (blue).

Funds were also used to purchase a spin coater which has been used to spin ionomer thin films (Nafion, SPEEK, and alkaline FAA-3) onto SiO<sub>2</sub> and Pt wafer surfaces. These samples can then be used for different types of reflectivity measurements, which include polarization modulated infrared reflection absorption spectroscopy, X-ray reflectometry, and neutron reflectometry. In PM-IRRAS, the combination of electric field enhancement and the surface selection rule, allows us to determine which functional groups are ordered by adsorption to the surface. The IR normal modes that have a transition moment perpendicular to the surface are enhanced. Previous results show that the SO<sub>3</sub><sup>-</sup> group and CF<sub>3</sub> groups are involved in the self-assembly of Nafion on Pt (Fig. 2). [2]

This is in contrast to SPEEK, which does not have the flexible side chain functional groups that Nafion contains. Instead the SO<sub>3</sub><sup>-</sup> group is located directly on the aromatic backbone, limiting the mobility of the hydrophilic/hydrophobic phase separation. PM-IRRAS of SPEEK thin films on Pt shows the enhancement of backbone normal modes, particularly COC stretching (Fig. 3). Interestingly, at this stage we do not see much PM-IRRAS enhancement SO<sub>3</sub><sup>-</sup> contribution to the interface.

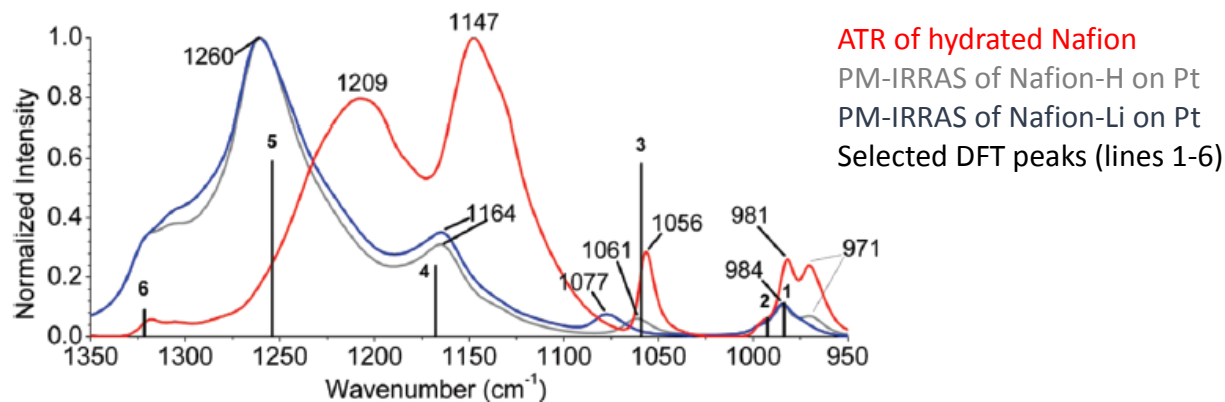


Figure 2. PM-IRRAS and ATR spectra of Nafion with selected DFT peaks.

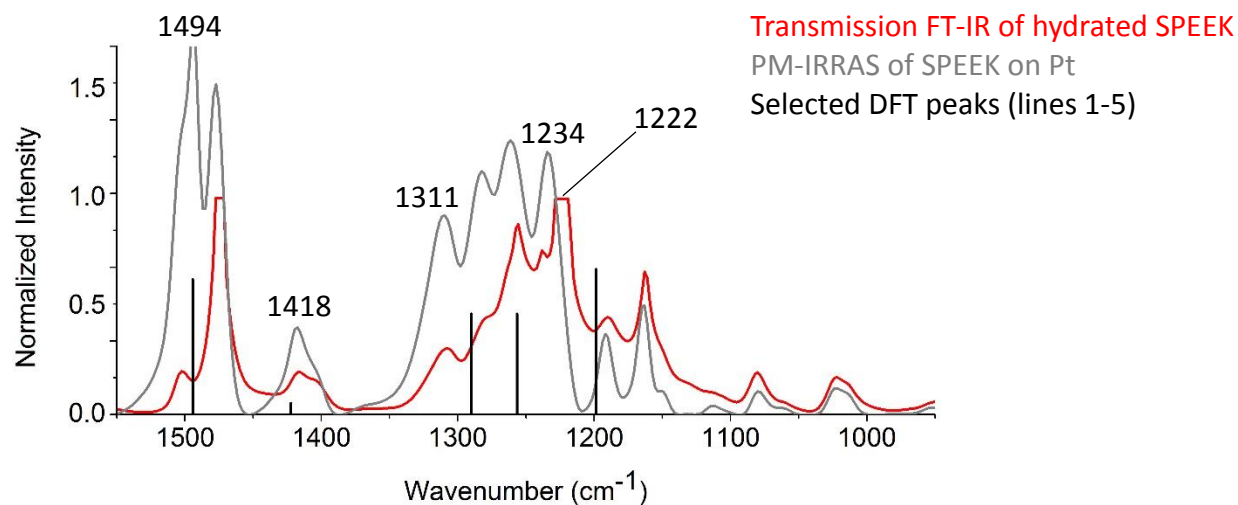


Figure 3. PM-IRRAS and transmission spectra of SPEEK with selected DFT peaks.

Neutron reflectometry results obtained at the NIST Center for Neutron Research in Gaithersburg, MD are currently being fitted (SPEEK on Pt and  $\text{SiO}_2$ ) (Fig. 4).

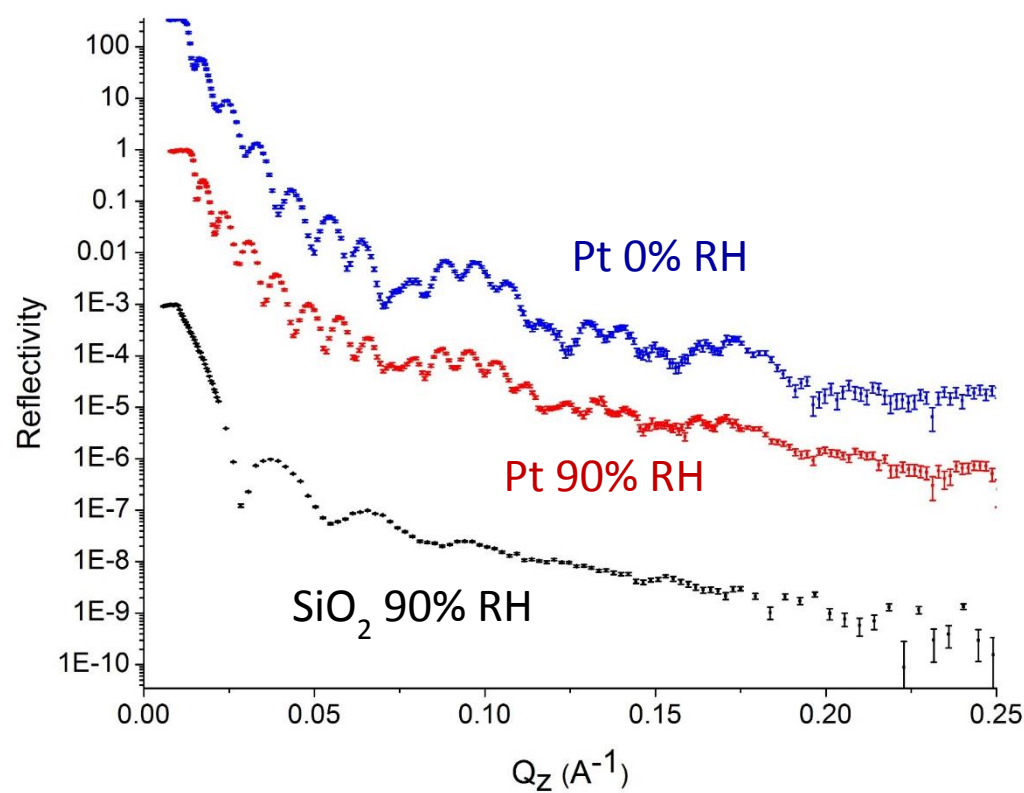


Figure 4. Neutron reflectivity data for SPEEK on  $\text{SiO}_2$  and Pt. .

The Agilent GC is currently being used to analyze results of a project involving isomerization of olefins through a flow reactor fuel cell. Typically,  $H_2$  is flowed through the anode of a fuel cell and  $O_2$  is flowed through the cathode of the fuel cell. The  $H_2$  dissociates into protons and electrons, with the protons travelling through an ionomer membrane (e.g., Nafion or SPEEK) to the cathode and the electrons travelling through an external circuit. The protons and electrons combine with the  $O_2$  at the cathode, producing current. In our setup, olefins are flowed through the cathode, where the protons are present at the catalytic layer. The olefins adsorb onto Pd and the protons cause isomerization, in the form of shifting double bonds, methyl groups, etc. The results are analyzed using the GC that was purchased

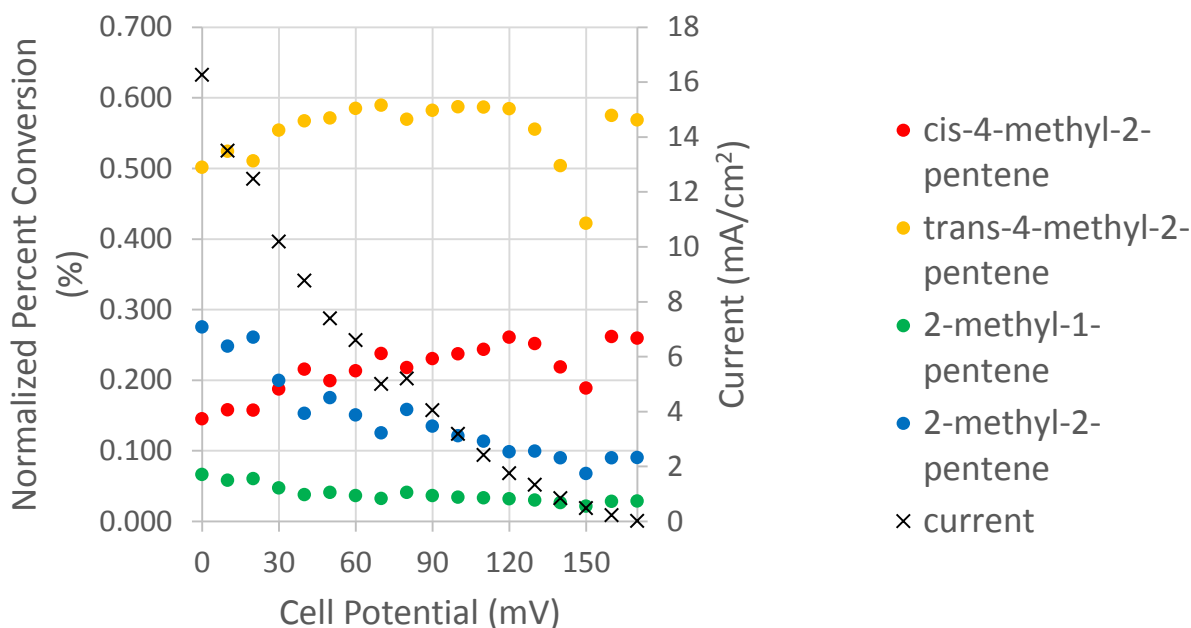


Figure 5. Percent conversion of 4-methyl-1-pentene versus cell potential

from the grant funding. Preliminary results show isomerization of 4 methyl 1 pentene, but we are in the process of reproducing the results and developing a better method of sampling to the GC. (Fig. 5)

### 3) Bibliography

1. Doan J, Navarro NE, Kumari D, Anderson K, Kingston E, Johnson C, Vong A, Dimakis N, and Smotkin ES. Polymer 2015;73:34-41.
2. Kendrick I, Kumari D, Yakaboski A, Dimakis N, and Smotkin ES. Journal of the American Chemical Society 2010;132(49):17611-17616.

Pictures of DURIP Equipment:



Agilent 6890N Gas Chromatograph





NuVant EZStat Pro

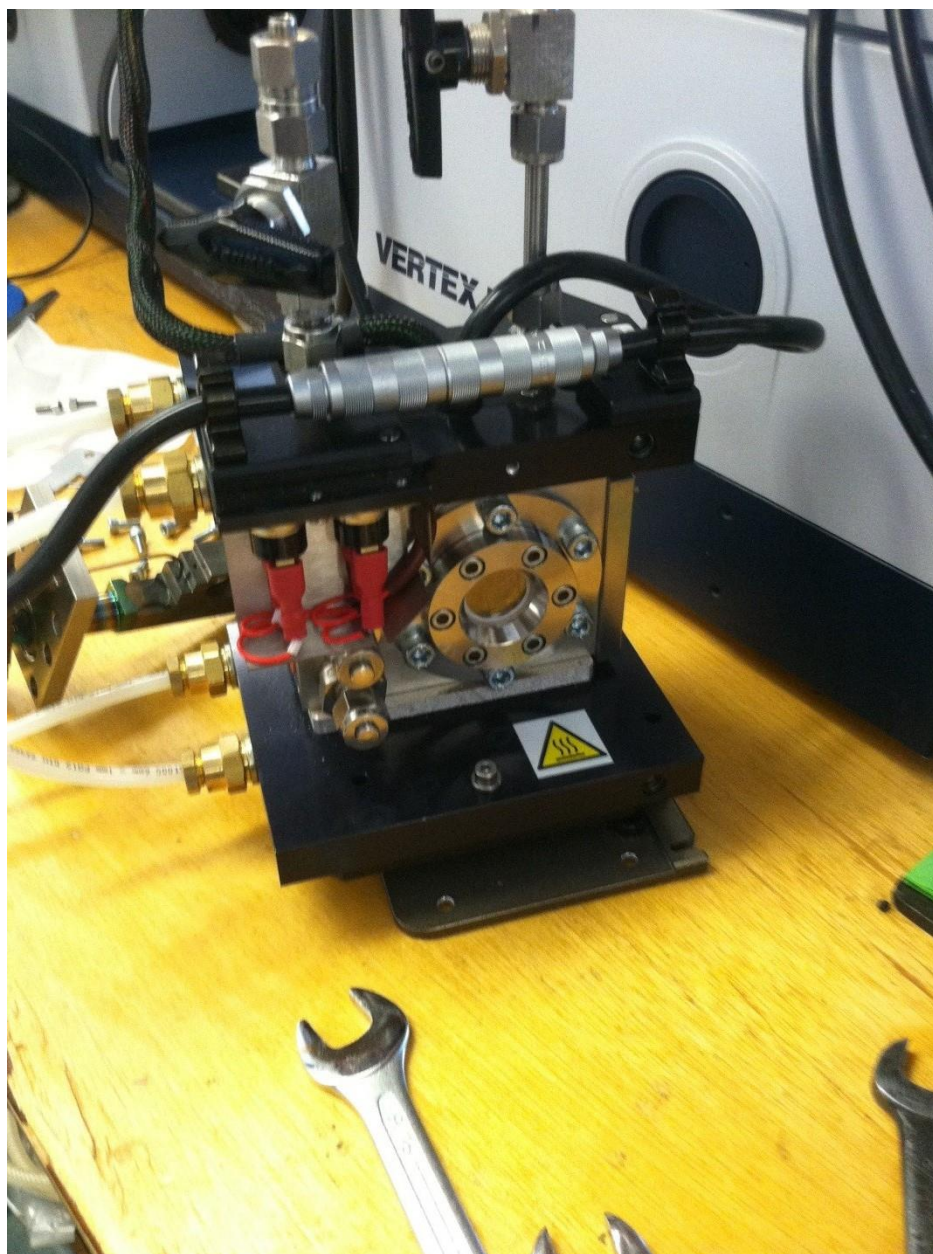


Rigaku X-ray Diffractometer



Replacement X-ray tube





SPECAC high-temperature/high pressure cell (View 1)



SPECAC high-temperature/high pressure cell (View 2)





MicroNano Tools Spincoater